

PA 1112425

## THE UNITED STATES OF AMERICA

TO ALL TO WHOM THESE PRESENTS SHALL COME:

UNITED STATES DEPARTMENT OF COMMERCE

United States Patent and Trademark Office

January 09, 2004

THIS IS TO CERTIFY THAT ANNEXED HERETO IS A TRUE COPY FROM THE RECORDS OF THE UNITED STATES PATENT AND TRADEMARK OFFICE OF THOSE PAPERS OF THE BELOW IDENTIFIED PATENT APPLICATION THAT MET THE REQUIREMENTS TO BE GRANTED A FILING DATE UNDER 35 USC 111.

APPLICATION NUMBER: 60/503,234

FILING DATE: September 16, 2003

REC'D 17 SEP 2004

WIPO PCT

**PRIORITY  
DOCUMENT**

SUBMITTED OR TRANSMITTED IN  
COMPLIANCE WITH RULE 17.1(a) OR (b)

By Authority of the  
COMMISSIONER OF PATENTS AND TRADEMARKS

*T. Wallace*  
T. WALLACE  
Certifying Officer

NOT AVAILABLE COPY

PATENT APPLICATION SERIAL NO. \_\_\_\_\_

U.S. DEPARTMENT OF COMMERCE  
PATENT AND TRADEMARK OFFICE  
FEE RECORD SHEET

09/18/2003 WABDELRI 00000108 082336 60503234  
01 FC:1005 160.00 DA

PTO-1556  
(5/87)

**PROVISIONAL APPLICATION FOR PATENT COVER SHEET**

This is a request for filing a PROVISIONAL APPLICATION FOR PATENT under 37 CFR 1.53(c).

Express Mail Label No.

ER132926907US

**INVENTOR(S)**

Given Name (first and middle [if any])	Family Name or Surname	Residence (City and either State or Foreign Country)
Luigi Paolo	Resconi Ferrari	Ferrara, Italy Ferrara, Italy

 Additional inventors are being named on the \_\_\_\_\_ separately numbered sheets attached hereto**TITLE OF THE INVENTION (500 characters max)****MULTISTEP PROCESS FOR PREPARING HETEROGENEOUS PROPYLENE COPOLYMERS**

Direct all correspondence to:

**CORRESPONDENCE ADDRESS** Customer Number

34872

Patent Trademark Office  
Barcode

OR

Type Customer Number here

34872

PATENT TRADEMARK OFFICE

 Firm or Individual Name

William R. Reid

Address

Basell USA Inc.

Address

912 Appleton Road

City

Elkton

State

MD

ZIP

21921

Country

US

Telephone

410-996-1783

Fax

410-996-1560

**ENCLOSED APPLICATION PARTS (check all that apply)** Specification Number of Pages

29

CD(s), Number

 Drawing(s) Number of Sheets Application Data Sheet. See 37 CFR 1.76

Other (specify)

**METHOD OF PAYMENT OF FILING FEES FOR THIS PROVISIONAL APPLICATION FOR PATENT** Applicant claims small entity status. See 37 CFR 1.27.FILING FEE  
AMOUNT (\$) A check or money order is enclosed to cover the filing fees

08-2336

 The Commissioner is hereby authorized to charge filing fees or credit any overpayment to Deposit Account Number:

\$160.00

 Payment by credit card. Form PTO-2038 is attached.

The invention was made by an agency of the United States Government or under a contract with an agency of the United States Government.

 No. Yes, the name of the U.S. Government agency and the Government contract number are: \_\_\_\_\_

Respectfully submitted,

SIGNATURE William R. Reid

Date 09/16/2003

TYPED or PRINTED NAME William R. Reid

REGISTRATION NO.  
(if appropriate)

TELEPHONE 410-996-1783

Docket Number:

47,894

FE 6129 (US)

**USE ONLY FOR FILING A PROVISIONAL APPLICATION FOR PATENT**

This collection of information is required by 37 CFR 1.51. The information is used by the public to file (and by the PTO to process) a provisional application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 8 hours to complete, including gathering, preparing, and submitting the complete provisional application to the PTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, Washington, D.C. 20231. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Box Provisional Application, Assistant Commissioner for Patents, Washington, D.C. 20231.

**EXPRESS MAILING CERTIFICATE**

This certifies that the attached **Form PTO/SB/16** (in duplicate), **Specification (29 pages)** for the provisional application of **Luigi Resconi et al.**, for **MULTISTEP PROCESS FOR PREPARING HETEROPHASIC PROPYLENE COPOLYMERS** (our ref: **FE 6129 (US)**) is being mailed by "Express Mail Post Office to Addressee" service in an envelope addressed:

Mail Stop Provisional Patent Application  
Commissioner for Patents  
P. O. Box 1450  
Alexandria, VA 22313-1450

and deposited on **September 16, 2003** as "Express Mail" in the United States Postal Service, the number of the "Express Mail" mailing label being **ER132926907US**.

Kyle Boulden

Typed Name of Person Mailing Paper or Fee



Signature of Person

**MULTISTEP PROCESS FOR PREPARING HETEROPHASIC PROPYLENE COPOLYMERS**

The present invention relates to a multistep process for preparing heterophasic propylene copolymers, by using a particular class of metallocene compounds.

5 Multistep processes for the polymerization of olefins, carried out in two or more reactors, are known from the patent literature and are of particular interest in industrial practice. The possibility of independently varying, in any reactors, process parameters such as temperature, pressure, type and concentration of monomers, concentration of hydrogen or other molecular weight regulator, provides much greater flexibility in controlling the composition and properties  
10 of the end product compared to single-step processes. Multistep processes are generally carried out using the same catalyst in the various steps/reactors. The product obtained in one reactor is discharged and sent directly to the next step/reactor without altering the nature of the catalyst.

US 5,854,354 discloses a multistep process in which a propylene polymer is prepared in step a) followed by an ethylene (co)polymer prepared in step b). In the Examples the  
15 metallocene-based catalyst system is not supported on a carrier but only prepolymerized. Therefore there is no control on the morphology of the obtained polymer.

US 5,753,773 discloses a multiphase block copolymer of propylene obtained by carrying out the polymerization in different stages without changing the catalyst system by changing the stage. The catalyst system comprises a metallocene compound supported on silica.

20 WO 01/48034 discloses in some examples a multistep process in which in the first step a propylene polymer is obtained and then, in the second step an ethylene/propylene polymer is produced. In all the examples of this document the metallocene-based catalysts are supported on silica.

A drawback of these processes is that the resulting polymers are often very sticky or in  
25 any case they have a poor flowability. Flowability can be measured according to a test reported in the examples that quantifies with a numerical scale (1-8) the tendency of the polymer particles to adhere to each other.

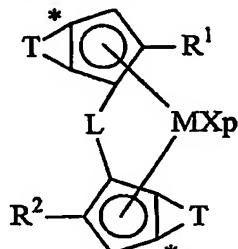
Thus it is desirable to have a process that permits to obtain heterophasic propylene  
30 polymer characterized by low values of flowability, so that to avoid fouling in the reactor and improve the processability of the obtained reactor blend.

This problem has been solved by the present invention by carrying out the whole process by using a metallocene-base catalyst system supported on a porous organic polymer.

An object of the present invention is a multistage process comprising the following steps:

5 a) polymerizing propylene with optionally one or more monomers selected from ethylene and alpha olefins of formula  $\text{CH}_2=\text{CHT}^1$ , wherein  $\text{T}^1$  is a  $\text{C}_2\text{-C}_{20}$  alkyl radical in the presence of a catalysts system, supported on a porous organic polymer, comprising:

i) one or more metallocene compounds of formula (I)



(I)

wherein:

10 M is an atom of a transition metal selected from those belonging to group 3, 4, 5, 6 or to the lanthanide or actinide groups in the Periodic Table of the Elements; preferably M is titanium, zirconium or hafnium;

p is an integer from 0 to 3, preferably p is 2, being equal to the formal oxidation state of the metal M minus 2;

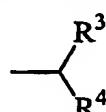
15 X, same or different, is a hydrogen atom, a halogen atom, or a R, OR,  $\text{OSO}_2\text{CF}_3$ , OCOR, SR, NR<sub>2</sub> or PR<sub>2</sub> group, wherein R is a linear or branched, saturated or unsaturated C<sub>1</sub>-C<sub>20</sub> alkyl, C<sub>3</sub>-C<sub>20</sub> cycloalkyl, C<sub>6</sub>-C<sub>20</sub> aryl, C<sub>7</sub>-C<sub>20</sub> alkylaryl or C<sub>7</sub>-C<sub>20</sub> arylalkyl radical, optionally containing heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements; or two X can optionally form a substituted or unsubstituted butadienyl radical or a OR'O group wherein R' is a divalent radical selected from C<sub>1</sub>-C<sub>20</sub> alkylidene, C<sub>6</sub>-C<sub>40</sub> arylidene, C<sub>7</sub>-C<sub>40</sub> alkylarylidene and C<sub>7</sub>-C<sub>40</sub> arylalkylidene radicals; preferably X is a hydrogen atom, a halogen atom or a R group; more preferably X is chlorine or a methyl radical;

20 L is a divalent bridging group selected from C<sub>1</sub>-C<sub>20</sub> alkylidene, C<sub>3</sub>-C<sub>20</sub> cycloalkylidene, C<sub>6</sub>-C<sub>20</sub> arylidene, C<sub>7</sub>-C<sub>20</sub> alkylarylidene, or C<sub>7</sub>-C<sub>20</sub> arylalkylidene radicals optionally containing heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements, and silylidene

radical containing up to 5 silicon atoms such as  $\text{SiMe}_2$ ,  $\text{SiPh}_2$ ; preferably L is selected from the group consisting of is  $\text{Si}(\text{CH}_3)_2$ ,  $\text{SiPh}_2$ ,  $\text{SiPhMe}$ ,  $\text{SiMe}(\text{SiMe}_3)$ ,  $\text{CH}_2$ ,  $(\text{CH}_2)_2$ ,  $(\text{CH}_2)_3$  and  $\text{C}(\text{CH}_3)_2$ ;

5  $\text{R}^1$ , is a linear or branched, saturated or unsaturated  $\text{C}_1\text{-C}_{40}$ -alkyl radical, optionally containing one or more heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements; preferably  $\text{R}^1$  is a methyl or ethyl radical;

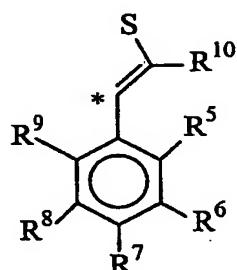
$\text{R}^2$  is a branched  $\text{C}_1\text{-C}_{40}$ -alkyl radical; preferably  $\text{R}^2$  is a group of formula (II)



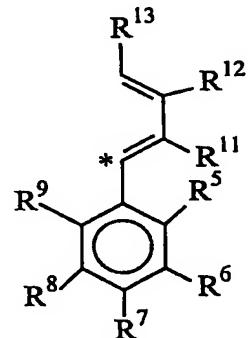
(II)

wherein  $\text{R}^3$  and  $\text{R}^4$ , equal to or different from each other, are linear or branched, saturated or unsaturated  $\text{C}_1\text{-C}_{10}$ -alkyl radicals optionally containing one or more heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements;

10  $\text{T}$ , equal to or different from each other, is a moiety of formula (IIIa) or (IIIb):



(IIIa)



(IIIb)

wherein:

the atom marked with the symbol \* is bonded to the atom marked with the same symbol in the compound of formula (I);

15  $\text{R}^5$ ,  $\text{R}^6$ ,  $\text{R}^7$ ,  $\text{R}^8$  and  $\text{R}^9$ , equal to or different from each other, are hydrogen atoms or a linear or branched, saturated or unsaturated  $\text{C}_1\text{-C}_{40}$ -alkyl,  $\text{C}_3\text{-C}_{40}$ -cycloalkyl,  $\text{C}_6\text{-C}_{40}$ -aryl,  $\text{C}_7\text{-C}_{40}$ -alkylaryl, or  $\text{C}_7\text{-C}_{40}$ -arylalkyl radicals, optionally containing one or more heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements; or two or more  $\text{R}^5$ ,  $\text{R}^6$ ,  $\text{R}^7$ ,

R<sup>8</sup> and R<sup>9</sup> can join to form a 4-7 saturated or unsaturated membered rings, said ring can bear C<sub>1</sub>-C<sub>20</sub> alkyl substituents;

R<sup>10</sup> is a hydrogen atom or a linear or branched, saturated or unsaturated C<sub>1</sub>-C<sub>20</sub>-alkyl, C<sub>3</sub>-C<sub>20</sub>-cycloalkyl, C<sub>6</sub>-C<sub>20</sub>-aryl, C<sub>7</sub>-C<sub>20</sub>-alkylaryl, or C<sub>7</sub>-C<sub>20</sub>-arylalkyl radicals, optionally

5 containing one or more heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements; preferably R<sup>10</sup> is a hydrogen atom or a linear or branched, saturated C<sub>1</sub>-C<sub>20</sub>-alkyl radical, such as a methyl, ethyl or isopropyl radical;

R<sup>11</sup>, R<sup>12</sup> and R<sup>13</sup>, equal to or different from each other, are hydrogen atoms or a linear or branched, saturated or unsaturated C<sub>1</sub>-C<sub>20</sub>-alkyl, C<sub>3</sub>-C<sub>20</sub>-cycloalkyl, C<sub>6</sub>-C<sub>20</sub>-aryl, C<sub>7</sub>-C<sub>20</sub>-

10 alkylaryl, or C<sub>7</sub>-C<sub>20</sub>-arylalkyl radicals, optionally containing one or more heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements; or two or more R<sup>11</sup>, R<sup>12</sup> and R<sup>13</sup> can join to form a 4-7 saturated or unsaturated membered rings, said ring can bear C<sub>1</sub>-C<sub>20</sub> alkyl substituents;

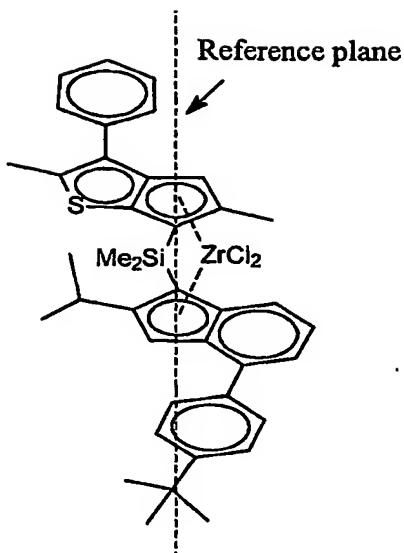
ii) an alumoxane or a compound capable of forming an alkyl metallocene cation; and optionally

15 iii) an organo aluminium compound;

b) contacting, under polymerization conditions, in a gas phase, ethylene with one or more alpha olefins of formula CH<sub>2</sub>=CHT<sup>2</sup>, wherein T<sup>2</sup> is a C<sub>1</sub>-C<sub>20</sub> alkyl radical, and optionally with a non-conjugated diene, in the presence of the polymer obtained in step a) and optionally in the presence of an additional organo aluminium compound.

20 The compound of formula (I) is preferably in the racemic or racemic-like form.

“Racemic-like” means that the benzo or thiophene moieties of the two  $\pi$ -ligands on the metallocene compound of formula (I) are on the opposite sides with respect to the plane containing the zirconium and the centre of the cyclopentadienyl moieties as shown in the following compound.



One preferred class of compounds of formula (I) is that wherein  $R^5$ ,  $R^6$ ,  $R^8$  and  $R^9$ , are hydrogen atoms and  $R^7$  is a group of formula  $-C(R^{14})_3$  wherein  $R^{14}$ , equal to or different from each other, are a linear or branched, saturated or unsaturated  $C_1$ - $C_{10}$ -alkyl,  $C_3$ - $C_{10}$ -cycloalkyl,  $C_6$ - $C_{10}$ -aryl,  $C_7$ - $C_{10}$ -alkylaryl, or  $C_7$ - $C_{10}$ -arylalkyl radicals, optionally containing one or more

5 heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements; preferably  $R^{14}$  are linear  $C_1$ - $C_{10}$ -alkyl radicals; more preferably they are methyl, or ethyl radicals.

A further preferred class of compounds of formula (I) is that wherein both T groups have formula (IIIb) and  $R^5$ ,  $R^6$ ,  $R^7$ ,  $R^8$  and  $R^9$  have the meaning described above. Preferably in one T group,  $R^{12}$  is a  $C_1$ - $C_{20}$  alkyl radical; preferably a  $C_1$ - $C_{10}$  alkyl radical; more preferably a methyl

10 or ethyl group and in the other T group  $R^{12}$  being hydrogen.

A further preferred class of compounds of formula (I) is that wherein one T group has formula (IIIa) and the other one has formula (IIIb) and  $R^5$ ,  $R^6$ ,  $R^7$ ,  $R^8$  and  $R^9$  have the meaning described above.

15 A still further preferred class of compounds of formula (I) is that wherein both T groups have formula (IIIb),  $R^5$ ,  $R^6$ ,  $R^7$ ,  $R^8$  and  $R^9$  have the meaning described above and  $R^{11}$ ,  $R^{12}$  and  $R^{13}$  are hydrogen atoms

Compounds of formula (I) are known in the art, for example they can be prepared according to the disclosure of WO 01/48034, PCT/EP02/13552 and DE 10324541.3

The porous polymer supports that can be used for the process of the present invention are porous polymers such as styrene/divinylbenzene copolymers, polyamides, or porous alpha-olefin polymers.

5 Preferably porous alpha-olefin polymers are used such as polyethylene, polypropylene, polybutene, copolymers of propylene and copolymers of ethylene.

Two particularly suitable classes of porous alpha-olefin polymers are those obtained according to WO 01/46272 and WO 02/051887 particularly good results are obtained when the catalyst described WO 01/46272 is used with the process described in WO 02/051887. Polymers obtained according to WO 01/46272 have a high content of the so-called stereoblocks, i.e. of

10 polymer fractions which, although predominantly isotactic, contain a not negligible amount of non-isotactic sequences of propylene units. In the conventional fractionation techniques such as the TREF (Temperature Rising Elution Temperature) those fractions are eluted at temperatures lower than those necessary for the more isotactic fractions. The polymers obtained according to the process described in WO 02/051887 show improved porosity.

15 The organic porous polymer has preferably porosity due to pores with diameter up 10  $\mu\text{m}$  (100000  $\text{\AA}$ ) measured to the method reported below, higher than 0.1 cc/g preferably comprised between 0.2 cc/g to 2 cc/g; more preferably from 0.3 cc/g to 1 cc/g.

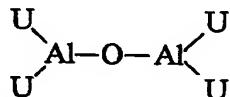
20 Preferably in the organic porous polymer fit as support according to the process of the present invention, the total porosity due to all pores whose diameter is comprised between 0.1  $\mu\text{m}$  (1000  $\text{\AA}$ ) and 2  $\mu\text{m}$  (20000  $\text{\AA}$ ) is at least 30% of the total porosity due to all pores whose diameter is comprised between 0.02  $\mu\text{m}$  (200  $\text{\AA}$ ) and 10  $\mu\text{m}$  (100000  $\text{\AA}$ ). Preferably the total porosity due to all pores whose diameter is comprised between 0.1  $\mu\text{m}$  (1000  $\text{\AA}$ ) and 2  $\mu\text{m}$  (20000  $\text{\AA}$ ) is at least 40% of the total porosity due to all pores whose diameter is comprised between 0.02  $\mu\text{m}$  (200  $\text{\AA}$ ) and 10  $\mu\text{m}$  (100000  $\text{\AA}$ ). More preferably the total porosity due all pores whose diameter is 25 comprised between 0.1  $\mu\text{m}$  (1000  $\text{\AA}$ ) and 2  $\mu\text{m}$  (20000  $\text{\AA}$ ) is at least 50% of the total porosity due all pores whose diameter is comprised between 0.02  $\mu\text{m}$  (200  $\text{\AA}$ ) and 10  $\mu\text{m}$  (100000  $\text{\AA}$ ).

30 The catalyst system supported on a porous organic polymer support used in the process of the present invention, can be obtained depositing the metallocene compound i) or the product of the reaction thereof with the component ii), or the component ii) and then the metallocene compound i) on the porous polymer support. The supportation process is carried out in an inert solvent such as hydrocarbon for example toluene, hexane, pentane or propane and at a temperature ranging from

0°C to 100°C, preferably the process is carried out at a temperature ranging from 25°C to 90°C. A preferred supportation process is described in WO 01/44319.

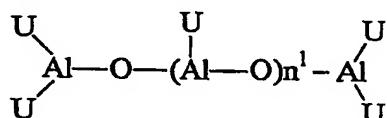
A particularly suitable process for supporting the catalyst system is described in WO01/44319, wherein the process comprises the steps of:

- 5     (a) preparing a catalyst solution comprising a catalyst system;
- (b) introducing into a contacting vessel:
- (i) a porous support material in particle form, and
- (ii) a volume of the catalyst solution not greater than the total pore volume of the porous support material introduced;
- 10    (c) discharging the material resulting from step (b) from the contacting vessel and suspending it in an inert gas flow, under such conditions that the solvent evaporates; and
- (d) reintroducing at least part of the material resulting from step (c) into the contacting vessel together with another volume of the catalyst solution not greater than the total pore volume of the reintroduced material.
- 15    The alumoxanes used in the catalyst according to the invention are considered to be linear, branched or cyclic compounds containing at least one group of the type:

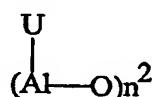


wherein the substituents U, same or different, are defined above.

In particular, alumoxanes of the formula:



- can be used in the case of linear compounds, wherein  $n^1$  is 0 or an integer of from 1 to 40 and the
- 20    substituents U are defined as above; or alumoxanes of the formula:



can be used in the case of cyclic compounds, wherein  $n^2$  is an integer from 2 to 40 and the U substituents are defined as above.

Examples of alumoxanes suitable for use according to the present invention are

methylalumoxane (MAO), tetra-(isobutyl)alumoxane (TIBAO), tetra-(2,4,4-trimethyl-pentyl)alumoxane (TIOAO), tetra-(2,3-dimethylbutyl)alumoxane (TDMBAO) and tetra-(2,3,3-trimethylbutyl)alumoxane (TTMBAO).

Particularly interesting cocatalysts are those described in WO 99/21899 and in WO01/21674

5 in which the alkyl and aryl groups have specific branched patterns.

Non-limiting examples of aluminium compounds that can be reacted with water to give suitable alumoxanes (b), described in WO 99/21899 and WO01/21674, are:

tris(2,3,3-trimethyl-butyl)aluminium, tris(2,3-dimethyl-hexyl)aluminium, tris(2,3-dimethyl-butyl)aluminium, tris(2,3-dimethyl-pentyl)aluminium, tris(2,3-dimethyl-heptyl)aluminium, tris(2-

10 methyl-3-ethyl-pentyl)aluminium, tris(2-methyl-3-ethyl-hexyl)aluminium, tris(2-methyl-3-ethyl-heptyl)aluminium, tris(2-methyl-3-propyl-hexyl)aluminium, tris(2-ethyl-3-methyl-butyl)aluminium, tris(2-ethyl-3-methyl-pentyl)aluminium, tris(2,3-diethyl-pentyl)aluminium, tris(2-propyl-3-methyl-butyl)aluminium, tris(2-isopropyl-3-methyl-butyl)aluminium, tris(2-isobutyl-3-methyl-pentyl)aluminium, tris(2,3,3-trimethyl-pentyl)aluminium, tris(2,3,3-trimethyl-hexyl)aluminium,

15 tris(2-ethyl-3,3-dimethyl-butyl)aluminium, tris(2-ethyl-3,3-dimethyl-pentyl)aluminium, tris(2-isopropyl-3,3-dimethyl-butyl)aluminium, tris(2-trimethylsilyl-propyl)aluminium, tris(2-methyl-3-phenyl-butyl)aluminium, tris(2-ethyl-3-phenyl-butyl)aluminium, tris(2,3-dimethyl-3-phenyl-butyl)aluminium, tris(2-phenyl-propyl)aluminium, tris[2-(4-fluoro-phenyl)-propyl]aluminium,

20 tris[2-(4-chloro-phenyl)-propyl]aluminium, tris[2-(3-isopropyl-phenyl)-propyl]aluminium, tris(2-phenyl-butyl)aluminium, tris(3-methyl-2-phenyl-butyl)aluminium, tris(2-phenyl-pentyl)aluminium, tris[2-(pentafluorophenyl)-propyl]aluminium, tris[2,2-diphenyl-ethyl]aluminium and tris[2-phenyl-2-methyl-propyl]aluminium, as well as the corresponding compounds wherein one of the hydrocarbyl groups is replaced with a hydrogen atom, and those wherein one or two of the hydrocarbyl groups are replaced with an isobutyl group.

25 Amongst the above aluminium compounds, trimethylaluminium (TMA), triisobutylaluminium (TIBA), tris(2,4,4-trimethyl-pentyl)aluminium (TIOA), tris(2,3-dimethylbutyl)aluminium (TDMBA) and tris(2,3,3-trimethylbutyl)aluminium (TTMBA) are preferred.

Non-limiting examples of compounds able to form an alkylmetallocene cation are 30 compounds of formula  $D^+E^-$ , wherein  $D^+$  is a Brønsted acid, able to donate a proton and to react irreversibly with a substituent X of the metallocene of formula (I) and  $E^-$  is a compatible anion,

which is able to stabilize the active catalytic species originating from the reaction of the two compounds, and which is sufficiently labile to be removed by an olefinic monomer. Preferably, the anion E<sup>-</sup> comprises one or more boron atoms. More preferably, the anion E<sup>-</sup> is an anion of the formula BAr<sub>4</sub><sup>(-)</sup>, wherein the substituents Ar which can be identical or different are aryl radicals such as phenyl, pentafluorophenyl or bis(trifluoromethyl)phenyl. Tetrakis-pentafluorophenyl borate is particularly preferred compound, as described in WO 91/02012. Moreover, compounds of formula BAr<sub>3</sub> can be conveniently used. Compounds of this type are described, for example, in the International patent application WO 92/00333. Other examples of compounds able to form an alkylmetallocene cation are compounds of formula BAr<sub>3</sub>P wherein P is a substituted or unsubstituted pyrrol radical. These compounds are described in WO01/62764. Compounds containing boron atoms can be conveniently supported according to the description of DE-A-19962814 and DE-A-19962910. All these compounds containing boron atoms can be used in a molar ratio between boron and the metal of the metallocene comprised between about 1:1 and about 10:1; preferably 1:1 and 2.1; more preferably about 1:1.

Non limiting examples of compounds of formula D<sup>+</sup>E<sup>-</sup> are:

- Triethylammoniumtetra(phenyl)borate,
- Tributylammoniumtetra(phenyl)borate,
- Trimethylammoniumtetra(tolyl)borate,
- Tributylammoniumtetra(tolyl)borate,
- 20 Tributylammoniumtetra(pentafluorophenyl)borate,
- Tributylammoniumtetra(pentafluorophenyl)aluminate,
- Tripropylammoniumtetra(dimethylphenyl)borate,
- Tributylammoniumtetra(trifluoromethylphenyl)borate,
- Tributylammoniumtetra(4-fluorophenyl)borate,
- 25 N,N-Dimethylbenzylammonium-tetrakis(pentafluorophenyl)borate,
- N,N-Dimethylhexylammonium-tetrakis(pentafluorophenyl)borate,
- N,N-Dimethylaniliniumtetra(phenyl)borate,
- N,N-Diethylaniliniumtetra(phenyl)borate,
- N,N-Dimethylaniliniumtetrakis(pentafluorophenyl)borate,
- 30 N,N-Dimethylaniliniumtetrakis(pentafluorophenyl)aluminate,
- N,N-Dimethylbenzylammonium-tetrakis(pentafluorophenyl)borate,

N,N-Dimethylhexylammonium-tetrakis(pentafluorophenyl)borate,  
Di(propyl)ammoniumtetrakis(pentafluorophenyl)borate,  
Di(cyclohexyl)ammoniumtetrakis(pentafluorophenyl)borate,  
Triphenylphosphoniumtetrakis(phenyl)borate,  
5 Triethylphosphoniumtetrakis(phenyl)borate,  
Diphenylphosphoniumtetrakis(phenyl)borate,  
Tri(methylphenyl)phosphoniumtetrakis(phenyl)borate,  
Tri(dimethylphenyl)phosphoniumtetrakis(phenyl)borate,  
Triphenylcarbeniumtetrakis(pentafluorophenyl)borate,  
10 Triphenylcarbeniumtetrakis(pentafluorophenyl)aluminate,  
Triphenylcarbeniumtetrakis(phenyl)aluminate,  
Ferroceniumtetrakis(pentafluorophenyl)borate,  
Ferroceniumtetrakis(pentafluorophenyl)aluminate.  
Triphenylcarbeniumtetrakis(pentafluorophenyl)borate, and  
15 N,N-Dimethylaniliniumtetrakis(pentafluorophenyl)borate.

Organic aluminium compounds used as compound iii) are those of formula  $H_jAlU_{3-j}$  or  $H_jAl_2U_{6-j}$  as described above.

Preferably step a) further comprises a prepolymerization step a-1).

The prepolymerization step a-1) can be carried out by contacting the catalyst system  
20 supported on the porous organic support with one or more alpha olefins of formula  $CH^2=CHT^3$   
wherein  $T^3$  is hydrogen or a  $C_1-C_{20}$  alkyl radical; preferably said alpha olefin is propylene or  
ethylene, at a temperature ranging from -20°C to 70°C, in order to obtain a prepolymerized  
catalyst system containing preferably from 5 to 500 g of polymer per gram of catalyst system.

Step a) of the present invention can be carried out in liquid phase, in which the  
25 polymerization medium can be an inert hydrocarbon solvent or the polymerization medium can be  
liquid propylene optionally in the presence of an inert hydrocarbon solvent, and of one or more  
comonomer of formula  $CH_2=CHT^1$ , or step a) can be carried out in a gas phase. Said hydrocarbon  
solvent can be either aromatic (such as toluene) or aliphatic (such as propane, hexane, heptane,  
isobutane, cyclohexane and 2,2,4-trimethylpentane).

Preferably the polymerization medium is liquid propylene. It can optionally contain minor amounts (up to 20% by weight, preferably up to 10% by weight, more preferably up to 5% by weight) of an inert hydrocarbon solvent or of one or more comonomer of formula  $\text{CH}_2=\text{CHT}^1$ .

Step a) can be carried out in the presence of hydrogen. The amount of hydrogen present during the polymerization reaction is preferably more than 1 ppm; more preferably from 5 to 2000 ppm; even more preferably from 6 to 500 ppm with respect to the propylene present in the reactor. Hydrogen can be added either at the beginning of the polymerization reaction or it can also be added at a later stage after a prepolymerization step has been carried out.

The propylene polymer obtained in step a) is a propylene homopolymer or a propylene copolymer containing up to 20% by mol preferably from 0.1 to 10% by mol, more preferably from 1% to 5% by mol of derived units of one or more alpha olefins of formula  $\text{CH}_2=\text{CHT}^1$ .

Non-limiting examples of alpha olefins of formula  $\text{CH}_2=\text{CHT}^1$  which can be used in the process of the invention are ethylene, 1-butene, 1-pentene, 4-methyl-1-pentene, 1-hexene, 1-octene, 4,6-dimethyl-1-heptene, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, 1-octadecene and 1-eicosene. Preferred comonomers are ethylene or 1-butene. Preferably in step a) a propylene homopolymer is produced.

The content of the polymer obtained in step a) ranges from 5% to 90% by weight of the polymer produced in the whole process, preferably it ranges from 10% to 70% by weight more preferably from 15% to 50% by weight of the total polymer produced in the whole process.

Step b) is carried out in a gas phase, preferably in a fluidized bed reactor. The polymerization temperature is generally comprised between -100°C and +200°C, and, preferably, between 10°C and +90°C. The polymerization pressure is generally comprised between 0,5 and 100 bar.

In step b) an ethylene copolymer containing from 5% to 90% by mol, preferably from 10% to 50% by mol, more preferably from 15% to 30% by mol of derived units of one or more alpha olefins of formula  $\text{CH}_2=\text{CHT}^2$  is produced. Examples of comonomer of formula  $\text{CH}_2=\text{CHT}^2$  that can be used in step b) of the present invention are: propylene, 1-butene, 1-pentene, 4-methyl-1-pentene, 1-hexene, 1-octene, 4,6-dimethyl-1-heptene, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, 1-octadecene and 1-eicosene. Preferred comonomers are propylene or 1-butene.

The content of polymer obtained in step b) preferably ranges from 10 to 95% by weight of the polymer produced in the whole process, preferably it ranges from 30% to 90% by weight and more preferably from 50% to 85% by weight.

5 The polymer obtained in step b) can optionally contain up to 20% by mol of a non conjugated diene. Non conjugated dienes can be a straight chain, branched chain or cyclic hydrocarbon diene having from 6 to 20 carbon atoms. Examples of suitable non-conjugated dienes are:

- straight chain acyclic dienes, such as 1,4-hexadiene and 1,6-octadiene;
- branched chain acyclic dienes, such as 5-methyl-1,4-hexadiene, 3,7-dimethyl-1,6-octadiene, 10 3,7-dimethyl-1,7-octadiene and mixed isomers of dihydro myricene and dihydroocinene;
- single ring alicyclic dienes, such as 1,3-cyclopentadiene, 1,4-cyclohexadiene, 1,5-cyclooctadiene and 1,5-cyclododecadiene;
- multi-ring alicyclic fused and bridged ring dienes, such as tetrahydroindene, methyl tetrahydroindene, dicyclopentadiene, bicyclo-(2,2,1)-hepta-2, 5-diene; and
- 15 - alkenyl, alkylidene, cycloalkenyl and cycloalkylidene norbornenes, such as 5-methylene-2-norbornene (MNB), 5-propenyl-2-norbornene, 5-isopropylidene-2-norbornene, 5-(4-cyclopentenyl)-2-norbornene, 5-cyclohexylidene-2-norbornene, 5-vinyl-2-norbornene and norbornadiene.

20 Preferred dienes are 1,4-hexadiene (HD), 5-ethylidene-2-norbornene (ENB), 5-vinylidene-2-norbornene (VNB), 5-methylene-2-norbornene (MNB) and dicyclopentadiene (DCPD). Particularly preferred dienes are 5-ethylidene-2-norbornene (ENB) and 1,4-hexadiene (HD).

25 When present the non-conjugated dienes are preferably incorporated into the polymer in an amount from 0.1% to about 20% by mol, preferably from 0.5% to 15% by mol, and more preferably from 0.5% to 7% by mol. If desired, more than one diene may be incorporated simultaneously, for example HD and ENB, with total diene incorporation within the limits specified above.

30 The process of the present invention can be carried out in one reactor or in two or more reactor in series.

30 In particular with the process of the present application heterophasic propylene polymers having excellent flowability and in high yields can be obtained. Flowability can be measured

according to the procedure reported below. This test gives a numeric value that measures the flowability index of the polymer.

Thus a further object of the present invention is a propylene polymer compositions obtainable according to the process of the present invention comprising:

5 a) 5% to 90% by weight, preferably from 10% to 70% by weight, more preferably from 15% to 50% by weight of a propylene homopolymer or a propylene copolymer containing up to 20% by mol preferably from 0.1 to 10% by mol, more preferably from 1% to 5% by mol of derived units of one or more alpha olefins of formula  $\text{CH}_2=\text{CHT}^1$ ; said propylene polymer or copolymer having isotactic pentads (mmmm) higher than 90%, preferably higher than 95% 10 more preferably higher than 97%;

b) from 10 to 95% by weight preferably from 30% to 90% by weight and more preferably from 50% to 85% by weight of an ethylene copolymer containing from 5% to 90% by mol, preferably from 10% to 50% by mol, more preferably from 15% to 30% by mol, of derived units of one or more alpha olefins of formula  $\text{CH}_2=\text{CHT}^2$ ;

15 said composition having a flowability index equal to or lower than 2.

The ethylene copolymer b) can further optionally contains up to 20% by mol of derived units of a non conjugated diene, preferably in an amount from 0.1% to about 20% by mol; more preferably from 0.5% to 15% by mol, and still more preferably from 0.5% to 7% by mol.

Preferred monomers to be copolymerized with ethylene in step b) are propylene and 1-butene.

The following examples are given to illustrate and not to limit the invention.

### Examples

#### **General characterization**

##### **Determination of X.S.**

25 2.5g of polymer were dissolved in 250 ml of o-xylene under stirring at 135°C for 30 minutes, then the solution was cooled to 25°C and after 30 minutes the insoluble polymer was filtered. The resulting solution was evaporated in nitrogen flow and the residue was dried and weighed to determine the percentage of soluble polymer (XS) and then, by difference, the insolubles (X.I.).

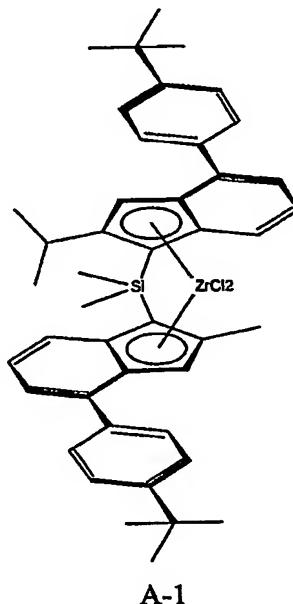
##### **NMR**

30 The proton and carbon spectra of polymers were obtained using a Bruker DPX 400 spectrometer operating in the Fourier transform mode at 120°C at 400.13 MHz and 100.61 MHz respectively.

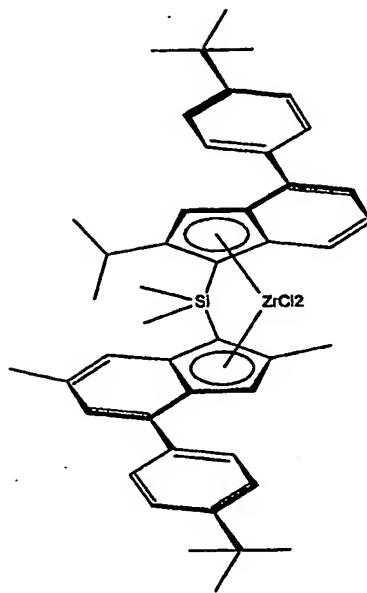
The samples were dissolved in C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>. As reference the residual peak of C<sub>2</sub>DHCl<sub>4</sub> in the <sup>1</sup>H spectra (5.95 ppm) and the peak of the *mmmm* pentad in the <sup>13</sup>C spectra (21.8 ppm) were used. Proton spectra were acquired with a 45° pulse and 5 seconds of delay between pulses; 256 transients were stored for each spectrum. The carbon spectra were acquired with a 90° pulse and 5 12 seconds (15 seconds for ethylene based polymers) of delay between pulses and CPD (waltz 16) to remove <sup>1</sup>H-<sup>13</sup>C couplings. About 3000 transients were stored for each spectrum. The intrinsic viscosity (I.V.) was measured in tetrahydronaphthalene (THN) at 135°C.

**Metallocene compounds**

rac-dimethylsilanediyl(2-methyl-4-(4'-tert-butylphenyl)indenyl)(2-isopropyl-4-(4'-tetr-butylphenyl)indenyl)zirconium dichloride (A-1) was prepared according to the procedure 10 described in WO 01/48034

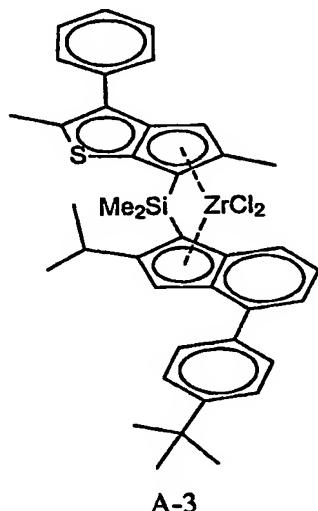


rac-dimethylsilanediyl(2,6-dimethyl-4-(4'-tert-butylphenyl)indenyl)(2-isopropyl-4-(4'-tetr-butylphenyl)indenyl)zirconium dichloride (A-2) was prepared according to the procedure described in DE 10324541.3



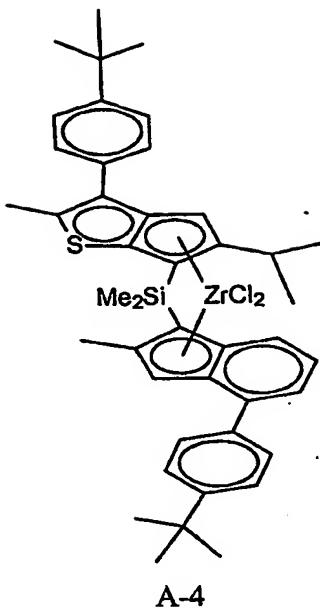
A-2

{Me<sub>2</sub>Si (4-(4-tert-Butyl-phenyl)-2-isopropyl-inden-1-yl)(2,5-dimethyl-3-phenyl-cyclopento[2,3-b]thiophen-6-yl)}ZrCl<sub>2</sub> (A-3) was prepared according to the procedure described in PCT/EP02/13552



A-3

{Me<sub>2</sub>Si (4-(4-tert-Butyl-phenyl)-2-isopropyl-inden-1-yl)(2,5-dimethyl-3-(4-tert-butyl-phenyl)-5 cyclopento[2,3-b]thiophen-6-yl)}ZrCl<sub>2</sub>. (A-4) was prepared according to the procedure described in PCT/EP02/13552.



### Porous organic polymer supports

Polypropylene prepolymer (support A) was produced according to the procedure described in the example 1 of WO 00/08065, under the following conditions: polymerisation temperature 20°C, AliBu<sub>3</sub> (AliBu<sub>3</sub>/ZN catalyst = 1 (w/w)), propylene flow = 1 kg/h for 2h, then 5 kg/h for 6h (conversion 40 g<sub>PP</sub>/g<sub>cat</sub>). Characterization data of the polymer are reported in table 1

5 Polyethylene prepolymer (support B) was produced according to the procedure described in example 1 of WO 95/26369, under the following conditions: polymerisation temperature 0°C, AliBu<sub>3</sub> (AliBu<sub>3</sub>/ZN catalyst = 1 (w/w)), 1.5 bar-g of ethylene (conversion of 40 g<sub>PE</sub>/g<sub>cat</sub>). Characterization data of the polymer are reported in table 1

Table 1			
Support	PBD g/ml	% of pores having diameter comprised between 0.1 µm (1000 Å) and 2 µm (20000 Å)	Porosity cc/g
A	0.262	69.93	0.585
B	0.626	64.51	0.663

### 10 Preparation of the catalyst systems

#### Catalyst C-1

4.6g of support B described above ,were treated with H<sub>2</sub>O dispersed in hexane in order to deactivate the MgCl<sub>2</sub>/Ti-based catalyst, then dried in a flow of nitrogen. The support is contacted with 0.5mL of MAO solution (30%w in toluene) diluted with 1.5 ml of toluene to scavenge impurities and residual water.

5 The catalytic complex was prepared by adding 42mg of metallocene (A-4) in 4.1ml of MAO solution (30% w/w in toluene).

The so obtained catalytic mixture is impregnated on support A (treated as described above) according to procedure described in WO 01/44319.

10 The obtained supported catalytic system contains 9.5 %w of Aluminium and 910 ppm of Zirconium measured via Ion Coupled Plasma.

#### Catalyst C-2

3.7g of support B described above ,were treated with H<sub>2</sub>O dispersed in hexane in order to deactivate the MgCl<sub>2</sub>/Ti-based catalyst, then dried in a flow of nitrogen. The support is contacted with 0.4mL of MAO solution (30%w in toluene) diluted with 1.6 ml of toluene to scavenge impurities and residual water.

15 The catalytic complex was prepared by adding 41mg of metallocene (A-3) in 4.3ml of MAO solution (30% w/w in toluene).

The so obtained catalytic mixture is impregnated on support B (treated as described above) according to procedure described in WO 01/44319.

20 The obtained supported catalytic system contains 13.4 %w of Aluminium and 1030 ppm of Zirconium measured via Ion Coupled Plasma.

#### Catalyst C-3

25 5.6g of support A described above ,were treated with H<sub>2</sub>O dispersed in hexane in order to deactivate the MgCl<sub>2</sub>/Ti-based catalyst, then dried in a flow of nitrogen. The support is contacted with 0.7mL of MAO solution (30%w in toluene) diluted with 1.3 ml of toluene to scavenge impurities and residual water.

The catalytic complex was prepared by adding 66mg of metallocenes (A-2) in 6.6ml of MAO solution (30% w/w in toluene).

30 The so obtained catalytic mixture is impregnated on support A (treated as described above) according to procedure described in WO 01/44319.

The obtained supported catalytic system contains 9.9%w of Aluminium and 0.10%w of Zirconium measured via Ion Coupled Plasma.

**Catalyst C-4**

5 5.0g of support A described above ,were treated with H<sub>2</sub>O dispersed in hexane in order to deactivate the MgCl<sub>2</sub>/Ti-based catalyst, then dried in a flow of nitrogen. The support is contacted with 0.5mL of MAO solution (30%w in toluene) diluted with 1.5 ml of toluene to scavenge impurities and residual water.

The catalytic complex was prepared by adding 89mg of metallocenes (K708) in 4.5ml of MAO solution (30% w/w in toluene).

10 The so obtained catalytic mixture is impregnated on support A (treated as described above) according to procedure described in WO 01/44319.

The obtained supported catalytic system contains 8.9%w of Aluminium and 0.14%w of Zirconium measured via Ion Coupled Plasma.

**Catalyst C-5 (comparative)**

15 3 kg of silica (Sylropol 948<sup>TM</sup>) is loaded in a process filter whose filter plate points upward, and suspended in 15 L of toluene. While stirring 7 L of a 30% strength by weight MAO solution are metered in at such a rate that the internal temperature does not exceed 35°C. After stirring for another 1 hour at a low stirrer speed, the process filter is turned that its filtration plate points downwards, the suspension is filtered, firstly under atmospheric pressure and then using 3 bar of nitrogen pressure. In parallel to the treatment of the support material, 2.0 L of 30% strength by weight MAO solution and 92.3 g of *rac*-dimethylsilylbis(2-methyl-4-(*para*-tert-butylphenyl)-indenyl)-zirconium dichloride are placed in a reaction vessel, the solution is stirred for 1 hour and allowed to settle for a further 30 minutes. The solution is subsequently added to the pretreated support material with the outlet closed. After addition is complete, the outlet is 20 opened and the filtrate is allowed to drain. When no more runs off, the outlet is closed, the filter cake is stirred for 15 minutes and allowed to rest for 1 hour. A nitrogen pressure of 3 bar is subsequently applied with the outlet open. 15 L of isododecane are added to the remaining solid, the mixture is stirred for 15 minutes and filtered. The washing step is repeated, and the solid is 25 subsequently pressed dry by means of a nitrogen pressure of 3 bar. For use in the polymerization, the total amount of the catalyst is resuspended in 15 L of isododecane.

30 The catalyst system contains 0.16%w of Zirconium.

**Catalyst C-6 (comparative)**

7.39 g of silica (XPO2107 from Grace) was dried at 180°C for 17 hours at a pressure of 15 mbar. Metallocene compound A-1 (24  $\mu$ mol) was dissolved in toluene ( 5 ml ) and stirred for 10 minutes, then 7.8 ml of a 30 % solution of methylalumoxane in toluene (MAO from

5 Albemarle) solution was added dropwise and color changed immediately from orange to ruby-red. the obtained suspension was stirred for 1 hour and then added dropwise to 1 g of dry silica gel purified as described above. The resulting suspension was stirred until a dark pink colour was obtained. The suspension was finally dried in vacuo for 1,5 hours at 50 °C. The resulting catalyst system contains .16 wt% of Zr, Al/Zr = 209

10 **Polymerization examples 1-7**

**General procedure**

All polymerization tests were carried out in a 4.250 L stainless steel Reactor, operated by a Yokogawa system, and equipped with a "ribbon" helical stirrer, with stirring rate of 300-400 RPM, a stainless steel vial for catalyst injection, and a look-through glass window.

15 **Step a)**

The reactor is purified by washing with 2L hexanes containing 5-6 mL TEA (triethylaluminium) 10% (1M), stirring 1 h at 70°C, and then discharging the solution through the bottom valve under N<sub>2</sub> pressure. The reactor temperature is lowered to 30°C, and the reactor pressure to 0.5 bar-g. Then the scavenger (4 mL 1M TEA in hexane) is added under a stream of 20 propylene, and 430 g of liquid propylene is added. The catalyst is added to the reactor through a stainless steel vial. For Polyethylene supported catalysts, the dry powder is loaded into the steel vial under N<sub>2</sub> stream, injected into the reactor by N<sub>2</sub> overpressure, then the vial rinsed with 3-4 mL of hexanes into the reactor, again with N<sub>2</sub> overpressure. For SiO<sub>2</sub> supported catalysts, the powder is added as a slurry in hexanes.

25 The homopolymer is produced in liquid monomer, by first a prepolymerization at 30°C for 5 min, then adding 100 NmL of H<sub>2</sub>, and the temperature is raised in 10 minutes at the polymerization temperature of 70°C and this temperature is kept constant until the pressure starts decreasing and no liquid phase is observed.

**Step b)**

30 Then the reactor is vented to 0.5 bar-g, the temperature is set at 60°C and the comonomers are fed in the ratio indicated in table 1, until a pressure of 25 bar-g is reached. The

comonomers are fed at constant temperature and pressure until 500 grams are taken in, or for a total polymerization time of two hours.

The polymerization is stopped by venting the monomers. The reactor is cooled, purged with N<sub>2</sub>, opened to inspect fouling, and the polymer is collected and dried in a vacuum oven at 5 60 °C for 1 hour. Polymerization data and characterisation of the obtained polymers are reported in table 2.

Table 2

Ex	cat. (mg)	step a)		step b)				kgCOP/ gcat/h
		time min.	yield g	C <sub>2</sub> g	C <sub>3</sub> g	C <sub>2</sub> /C <sub>3</sub> mol ratio	time min.	
1	C-2 (307)	40	149	34	135	0.38	95	1.0
2	C-1 (411)	30	96	79	46	2.58	117	0.6
3	C-4 (440)	13	128	34	135	0.38	51	1.3
4*	C-6 (205)	24	120	34	156	0.33	71	2.1
5	C-3 (328)	20	210	34	135	0.38	159	0.6
5	C-3 (351)	25	140	61	81	1.13	126	0.7
7*	C-5 (170)	40	190	61	81	1.13	81	2.2

\* comparative

Table 2 (continued)

Ex	IV <sub>(THN)</sub>	split#	XS	IV <sub>(XS)</sub>	XI	C <sub>2,copo</sub> NMR	mmmm
							homopolymer
	dl/g	%wt	% wt	dl/g	% wt	%wt	>97%
1	1.33	77	76	1.5	24	25.7	>97%
2	2.05	84	74	2.4	26	55.4	>97%
3	1.7	79.6	74	1.8	25.9	24.2	>97%
4*	1.9	81	80.7	2	19.3	25.8	>97%
5	2	70.4	66	2.3	33.7	23.0	>97%
7*	n.a.	72	n.a.	n.a.	n.a.	47.6	>97%

\* comparative

n.a. not available

# rubber content in the composition

#### Flowability test

10 A flowability test was designed to compare the behaviour of particles of soft and sticky materials. The degree of flowability is rated on a scale of 1 to 8. 1-2 means no clumping hence good flowability, 3 to 7 means increasing clumping hence poor flowability, 8 means a solid clump hence no flowability at all. The test procedure is the following:

Equipment : a 50 mm diameter PMMA cylinder (h 150 mm)  
 weights to supply an even pressure on the surface of the cylinder  
 an open-air flow vented oven.

## Procedure:

- 5 1) place the cylinder on a tray
- 2) fill the cylinder with enough polymer to obtain a solid bed with height of 100 mm
- 3) vibrate the cylinder to allow particles to settle. Additional particles are added if the solid height decreases
- 4) place the sample in oven at 40°C for 2 hours
- 10 5) remove sample from the oven and carefully lift the cylinder from around the particles. The particles may fall out of the cylinder or maintain the shape of the cylinder.
- 6) in this last case, increasing weight is added on a plate put on the top of the solid block, until the particles or clumps fall apart

the behaviour is rated according to the rules reported in table 3. The results of the test carried out on samples of the polymers obtained in examples 1-7 are reported in table 4.

- 15

Table 3

rate	behaviour
1	once lift the cylinder the particles don't stuck together and fall apart, even if some clumping are present
2	once lift the cylinder the particles stay with the shape of the cylinder but after putting a weight up to 70g evenly distributed with a plate on the top of the solid block, the particles fall apart in a time < 100 sec
3	as 2, but the breaking of the clump requires a time > 100 sec
4	as 2, but to break the particles block the weight has to be increased up to 80 g and the particles fall apart in < 100 sec
5	as 4, but the breaking of the clump happens after a time > 100 sec
6	as 4, but to break the particles block the weight has to be increased up to 100 g and the particles fall apart in < 100 sec
7	as 6 but the breaking is slow and requires > 100 sec.
8	the particles are completely clumped and a weight > 150 g is required to break apart the clumps.

Table 4

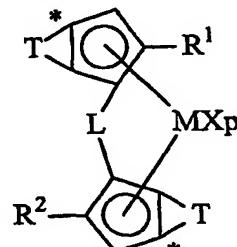
sample	% split	% w C <sub>2</sub> copo	flowability
1	77	25.7	2
2	84	55.4	1
3	79.6	24.2	1
4*	81	25.8	7
5	70.4	23	1
7*	72	47.6	5

Claims

1. A multistage process comprising the following steps:

5 step a) polymerizing propylene with optionally one or more monomers selected from ethylene and alpha olefins of formula  $\text{CH}_2=\text{CHT}^1$ , wherein  $\text{T}^1$  is a  $\text{C}_2\text{-C}_{20}$  alkyl radical in the presence of a catalysts system, supported on a porous organic polymer, comprising:

i) one or more metallocene compounds of formula (I)



(I)

wherein:

10 M is an atom of a transition metal selected from those belonging to group 3, 4, 5, 6 or to the lanthanide or actinide groups in the Periodic Table of the Elements;

p is an integer from 0 to 3, being equal to the formal oxidation state of the metal M minus 2;

15 X, same or different, is a hydrogen atom, a halogen atom, or a R, OR,  $\text{OSO}_2\text{CF}_3$ , OCOR, SR, NR<sub>2</sub> or PR<sub>2</sub> group, wherein R is a linear or branched, saturated or unsaturated  $\text{C}_1\text{-C}_{20}$  alkyl,  $\text{C}_3\text{-C}_{20}$  cycloalkyl,  $\text{C}_6\text{-C}_{20}$  aryl,  $\text{C}_7\text{-C}_{20}$  alkylaryl or  $\text{C}_7\text{-C}_{20}$  arylalkyl radical, optionally containing heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements; or two X can optionally form a substituted or unsubstituted butadienyl radical or a OR'O group wherein R' is a divalent radical selected from  $\text{C}_1\text{-C}_{20}$  alkylidene,  $\text{C}_6\text{-C}_{40}$  arylidene,  $\text{C}_7\text{-C}_{40}$  alkylarylidene and  $\text{C}_7\text{-C}_{40}$  arylalkylidene radicals;

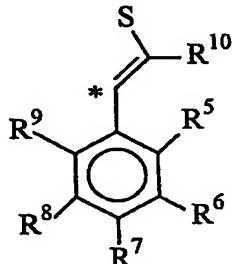
20 L is a divalent bridging group selected from  $\text{C}_1\text{-C}_{20}$  alkylidene,  $\text{C}_3\text{-C}_{20}$  cycloalkylidene,  $\text{C}_6\text{-C}_{20}$  arylidene,  $\text{C}_7\text{-C}_{20}$  alkylarylidene, or  $\text{C}_7\text{-C}_{20}$  arylalkylidene radicals optionally containing heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements, and silylidene radical containing up to 5 silicon atoms;

$R^1$ , is a linear or branched, saturated or unsaturated  $C_1$ - $C_{40}$ -alkyl radical, optionally containing one or more heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements;

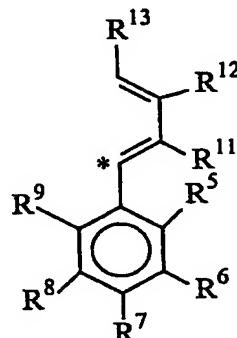
$R^2$  is a branched  $C_1$ - $C_{40}$ -alkyl radical;

5

$T$ , equal to or different from each other, is a moiety of formula (IIIa) or (IIIb):



(IIIa)



(IIIb)

wherein:

the atom marked with the symbol \* is bonded to the atom marked with the same symbol in the compound of formula (I);

10

$R^5$ ,  $R^6$ ,  $R^7$ ,  $R^8$  and  $R^9$ , equal to or different from each other, are hydrogen atoms or a linear or branched, saturated or unsaturated  $C_1$ - $C_{40}$ -alkyl,  $C_3$ - $C_{40}$ -cycloalkyl,  $C_6$ - $C_{40}$ -aryl,  $C_7$ - $C_{40}$ -alkylaryl, or  $C_7$ - $C_{40}$ -arylalkyl radicals, optionally containing one or more heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements; or two or more  $R^5$ ,  $R^6$ ,  $R^7$ ,  $R^8$  and  $R^9$  can join to form a 4-7 saturated or unsaturated membered rings, said ring can bear  $C_1$ - $C_{20}$  alkyl substituents;

15

$R^{10}$  is a hydrogen atom or a linear or branched, saturated or unsaturated  $C_1$ - $C_{20}$ -alkyl,  $C_3$ - $C_{20}$ -cycloalkyl,  $C_6$ - $C_{20}$ -aryl,  $C_7$ - $C_{20}$ -alkylaryl, or  $C_7$ - $C_{20}$ -arylalkyl radicals, optionally containing one or more heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements;

20

$R^{11}$ ,  $R^{12}$  and  $R^{13}$ , equal to or different from each other, are hydrogen atoms or a linear or branched, saturated or unsaturated  $C_1$ - $C_{20}$ -alkyl,  $C_3$ - $C_{20}$ -cycloalkyl,  $C_6$ - $C_{20}$ -aryl,  $C_7$ - $C_{20}$ -alkylaryl, or  $C_7$ - $C_{20}$ -arylalkyl radicals, optionally containing one or more heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements;

or two or more R<sup>11</sup>, R<sup>12</sup> and R<sup>13</sup> can join to form a 4-7 saturated or unsaturated membered rings, said ring can bear C<sub>1</sub>-C<sub>20</sub> alkyl substituents;

- ii) an alumoxane or a compound capable of forming an alkyl metallocene cation;

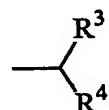
5 step b) contacting, under polymerization conditions, in a gas phase, ethylene with one or more alpha olefins of formula CH<sub>2</sub>=CHT<sup>2</sup>, wherein T<sup>2</sup> is a C<sub>1</sub>-C<sub>20</sub> alkyl radical, and optionally with a non-conjugated diene, in the presence of the polymer obtained in step a).

2. The multistage process according to claim 1 wherein step b) is carried out in the presence of an additional organo aluminium compound.

10 3. The multistage process according to claims 1 or 2 wherein the catalyst system further comprises iii) an organo aluminium compound.

4. The multistage process according to anyone of claims 1-3 wherein M is titanium, zirconium or hafnium; X is a hydrogen atom, a halogen atom or a R group wherein R is a linear or branched, saturated or unsaturated C<sub>1</sub>-C<sub>20</sub> alkyl, C<sub>3</sub>-C<sub>20</sub> cycloalkyl, C<sub>6</sub>-C<sub>20</sub> aryl, C<sub>7</sub>-C<sub>20</sub> alkylaryl or C<sub>7</sub>-C<sub>20</sub> arylalkyl radical, optionally containing heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements; L is selected from Si(Me)<sub>2</sub>, SiPh<sub>2</sub>, SiPhMe, SiMe(SiMe<sub>3</sub>), CH<sub>2</sub>, (CH<sub>2</sub>)<sub>2</sub>, (CH<sub>2</sub>)<sub>3</sub> and C(CH<sub>3</sub>)<sub>2</sub>.

15 5. The multistage process according to anyone of claims 1-4 wherein R<sup>1</sup> is a methyl or ethyl radical; R<sup>2</sup> is a group of formula (II)



(II)

20 wherein R<sup>3</sup> and R<sup>4</sup>, equal to or different from each other, are linear or branched, saturated or unsaturated C<sub>1</sub>-C<sub>10</sub>-alkyl radicals optionally containing one or more heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements; and R<sup>10</sup> is a hydrogen atom or a linear or branched, saturated C<sub>1</sub>-C<sub>20</sub>-alkyl radical.

6. The multistage process according to anyone of claims 1 to 5 wherein the compound of formula (I) R<sup>5</sup>, R<sup>6</sup>, R<sup>8</sup> and R<sup>9</sup>, are hydrogen atoms and R<sup>7</sup> is a group of formula -C(R<sup>14</sup>)<sub>3</sub> wherein R<sup>14</sup>, equal to or different from each other, are a linear or branched, saturated or unsaturated C<sub>1</sub>-C<sub>10</sub>-alkyl, C<sub>3</sub>-C<sub>10</sub>-cycloalkyl, C<sub>6</sub>-C<sub>10</sub>-aryl, C<sub>7</sub>-C<sub>10</sub>-alkylaryl, or C<sub>7</sub>-C<sub>10</sub>-

arylalkyl radicals, optionally containing one or more heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements.

7. The multistage process according to claim 6 wherein in the compound of formula (I) both T groups have formula (IIIb).

5 8. The multistage process according to claim 7 wherein in the compound of formula (I) in one T group, R<sup>12</sup> is a C<sub>1</sub>-C<sub>20</sub> alkyl radical; and in the other T group R<sup>12</sup> being hydrogen.

9. The multistage process according to claim 6 wherein in the compound of formula (I) one T group has formula (IIIa) and the other one has formula (IIIb).

10. The multistage process according to claim 6 wherein in the compound of formula (I) both T groups have formula (IIIb) and R<sup>11</sup>, R<sup>12</sup> and R<sup>13</sup> are hydrogen atoms.

11. The multistage process according to anyone of claims 1 to 10 wherein the organic porous polymer has preferably porosity due to pores with diameter up 10 µm (100000 Å) higher than 0.1 cc/g.

12. The multistage process according to claim 11 wherein in the organic porous polymer the total porosity due to all pores whose diameter is comprised between 0.1 µm (1000 Å) and 2 µm (20000 Å) is at least 30% of the total porosity due to all pores whose diameter is comprised between 0.02 µm (200 Å) and 10 µm (100000 Å).

13. The multistage process according to anyone of claims 1-12 wherein:

20 in step a) from 5% to 90% by weight, with respect to the polymer produced in the whole process, of a propylene homopolymer or a propylene copolymer containing up to 20% by mol of derived units of one or more alpha olefins of formula CH<sub>2</sub>=CHT<sup>1</sup> is produced, wherein T<sup>1</sup> is a C<sub>2</sub>-C<sub>20</sub> alkyl radical; and

25 in step b) from 10 to 95% by weight, with respect to the polymer produced in the whole process, an ethylene copolymer containing from 5% to 90% by mol, of derived units of one or more alpha olefins of formula CH<sub>2</sub>=CHT<sup>2</sup> is produced, wherein T<sup>2</sup> is a C<sub>1</sub>-C<sub>20</sub> alkyl radical.

14. The multistage process according to claim 13 wherein the ethylene copolymer obtained in step b) contains up to 20% by mol of a non conjugated diene.

15. The multistage process according to claims 13 or 14 wherein in step a) a propylene homopolymer is produced.

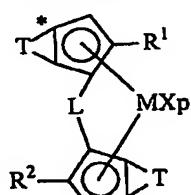
16. The multistage process according to anyone of claims 13-15 wherein in step b) comonomers are selected from propylene and 1-butene.
17. A propylene polymer compositions obtainable according to the process of anyone of claims 1-17 comprising:
  - 5 a) 5% to 90% by weight, of a propylene homopolymer or a of propylene copolymer containing up to 20% by mol of derived units of one or more alpha olefins of formula  $\text{CH}_2=\text{CHT}^1$  wherein  $\text{T}^1$  is a  $\text{C}_2\text{-C}_{20}$  alkyl radical; said propylene polymer or copolymer having isotactic pentads (mmmm) higher than 90%;
  - b) from 10 to 95% by weight of an ethylene copolymer containing from 5% to 90% by mol, of derived units of one or more alpha olefins of formula  $\text{CH}_2=\text{CHT}^2$  wherein  $\text{T}^2$  is a  $\text{C}_1\text{-C}_{20}$  alkyl radical;  
10 said composition having a flowability index equal to or lower than 2.

**Abstract**

A multistage process for obtaining an heterophasic propylene polymer comprising the following steps:

5 step a) contacting under polymerization conditions propylene and optionally ethylene or one or more alpha olefins in the presence of a catalysts system, supported on a porous organic polymer, comprising:

ii) one or more metallocene compounds of formula (I)

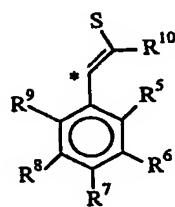


(I)

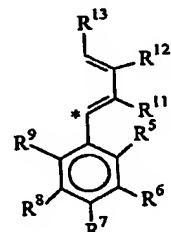
wherein:

10 M is an atom of a transition metal; p is an integer from 0 to 3; X, same or different, is a hydrogen atom, a halogen atom, or a hydrocarbon group; L is a divalent bridging group; R<sup>1</sup>, is a linear or branched, saturated or unsaturated C<sub>1</sub>-C<sub>20</sub>-alkyl radical; R<sup>2</sup> is a branched C<sub>1</sub>-C<sub>20</sub>-alkyl radical;

T, equal to or different from each other, is a moiety of formula (IIIa) or (IIIb):



(IIIa)



(IIIb)

wherein:

15 the atom marked with the symbol \* bonds the atom marked with the same symbol in the compound of formula (I);

R<sup>5</sup>-R<sup>13</sup>, equal to or different from each other, are hydrogen atoms or hydrocarbon groups;

- ii) an alumoxane or a compound capable of forming an alkyl metallocene cation; and  
optionally
- iii) an organo aluminium compound;

5 step b) contacting, under polymerization conditions, in a gas phase, ethylene and one or more alpha olefins and optionally a non-conjugated diene, in the presence of the polymer obtained in step a) and optionally in the presence of an additional organo aluminium compound.

**This Page is Inserted by IFW Indexing and Scanning  
Operations and is not part of the Official Record**

## **BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

**BLACK BORDERS**

**IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**

**FADED TEXT OR DRAWING**

**BLURRED OR ILLEGIBLE TEXT OR DRAWING**

**SKEWED/SLANTED IMAGES**

**COLOR OR BLACK AND WHITE PHOTOGRAPHS**

**GRAY SCALE DOCUMENTS**

**LINES OR MARKS ON ORIGINAL DOCUMENT**

**REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**

**OTHER:** \_\_\_\_\_

**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.**